DOCKET NO: 248810US2CONT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF   :

GEOFFREY ALAN SCARSBROOK, ET   : EXAMINER: MONDT

AL

SERIAL NO: 10/777,633   :

FILED: FEBRUARY 13, 2004   : GROUP ART UNIT: 3663

FOR: SINGLE CRYSTAL DIAMOND   :

PREPARED BY CVD

DECLARATION UNDER 37 CFR 1.132

1. I, Geoffrey Alan Scarsbrook of 40 Cavendish Meads, Sunninghill, Ascot, SL5 9TD, Berkshire, United Kingdom, hereby declare that I am an original, first and joint inventor of the subject matter of US application 10/777,633 entitled "Single Crystal Diamond Prepared by CVD" (hereinafter the present specification).

2. I have reviewed the Office Action dated March 15, 2006, and in particular the Examiner's rejection of claims under 35 U.S.C. 103(a) as unpatentable over Marinelli et al, High-quality diamond growth by chemical-vapor deposition: Improved collection efficiency

in α-particle detection, *Appl. Phys. Lett.*, Vol. 75, No. 20, pp.3216-18 (1999) (Marinelli et al) combined with US 5,443,032 (Vichr et al) alone, and with additional prior art.

3. In the Office Action, the Examiner finds that Marinelli et al "implies" a charge collection distance (CCD) of "about" 150 μm at an applied field of 1 V/μm for an "almost" single crystal diamond based on Marinelli et al's disclosure of their films being "almost free of grain boundaries", combined with Equation (3) and Fig. 2 therein, which the Examiner interprets as showing an efficiency at 1 V/μm of about 60% of the efficiency at, in effect, 4 V/μm. The Examiner also finds that it would have been obvious to remove the portion in Marinelli et al not almost free of grain boundaries to increase CCD. The Examiner further finds that US 5,443,032 (Vichr et al '032) suggests using a CVD method that results in single-crystal diamond in the first place as the method in Marinelli et al. The Examiner relies on US 5,803,967 (Plano et al) to suggest that practicing the surface etching therein would result in a CCD according to Claims 11 and 12.

4. I was advised that a personal interview was conducted with the Examiner in charge of this application and have subsequently been advised to submit a declaration that would explain why the presently-claimed invention is not suggested by, and would not have been obvious over, the above applied prior art references. To that end, the following is offered.

5. With regard to Marinelli et al, there are two areas that require clarification. The first is the description of the material and the second is the quoted CCD values and how they are interpreted.

Structure (single crystal compared with polycrystalline)

Marinelli et al reports measurements made on polycrystalline CVD diamond. The first point to make is that this material is quite distinct from single crystal diamond. Single crystal CVD diamond is produced by homoepitaxial growth on a single crystal diamond substrate, and is **completely** free of grain boundaries within the whole volume of the sample. Expressed another way, the crystal lattice of a single crystal is continuous and not disrupted by two-dimensional features (i.e. grain boundaries) across the whole sample. In contrast, CVD polycrystalline diamond is grown on a non-diamond substrate, Marinelli et al used silicon, with multiple nucleation sites on the substrate (typically more than 10^6 cm^{-2}) and with a typical grain size at the nucleation face of less than 1 μm. During growth of the layer, grain competition (due to variation in growth rate with crystallographic orientation) results in fewer, larger grains, with typically the lateral grain size at any point being about 10% of the thickness of the layer, but with the grain boundaries extending throughout the thickness of the layer. Indeed, a 115 μm thick film would be expected to have an average grain size of ~10-15 μm. Simple math shows that at 15 μm grain size, this is equivalent to a length of grain boundaries of about 6×10^6 cm per cm^2 of surface (or about 2×10^6 cm per cm^2 of surface for 50 μm grain size). This should be compared with zero in a single crystal CVD diamond.

Further, whilst the grains may be reasonably well (but not perfectly) crystallographically aligned parallel to the growth direction as a result of the competitive growth surface, they are rotated randomly about growth direction, possessing what is described in the art as a 'wire texture'. The grain boundaries then define the boundaries between adjacent crystals with very different orientation, and the grain boundary cannot simply disappear.

In consequence, to say a polycrystalline diamond film is 'almost free of grain boundaries' is incorrect and grossly misleading, particularly taken out of its intended context which is the comparison of one polycrystalline diamond layer with another.

What is true is that a path through the thickness of the layer (in the direction of growth) can be found which does not intersect a grain boundary for a distance substantial in comparison to the layer thickness, but that in contrast, parallel to the major surfaces of the film, a much shorter path will intersect many grain boundaries. Furthermore, whilst a selected path in the growth direction may extend a considerable distance without crossing a grain boundary, there is substantial variation for randomly selected paths, which results in the spread of charge collection efficiencies reported in Figure 1, which shows minimum values of 20% to maximum values of 70%. Consequently, the properties of polycrystalline diamond do not show the high symmetry of the cubic diamond lattice, but have a strongly preferred direction which is parallel to the growth direction and are highly non-uniform in electronic properties (including CCD) across the sample depending on whether a particular path is close/intersects a grain boundary or is centred between them.

Polycrystalline CVD diamond is quite distinct from single crystal CVD diamond, the properties of polycrystalline diamond being substantially limited by the grain boundaries, and polycrystalline diamond does not slowly become single crystal diamond with thickness, despite the misleading comments by Marinelli et al.

Marinelli et al's comment at the end of page 3218 that:

> because our films are almost free of grain boundaries for most of their thickness, increasing the thickness and removing the highly defective interface layer could reasonably lead to extremely high charge collection distances

glosses over a number of points:

a)   as stated earlier, the layer remains polycrystalline and therefore contains grain boundaries throughout its thickness,

b)   it is assumed by the examiner that they can grow much thicker layers, which is not demonstrated. This cannot be assumed as the quality of polycrystalline diamond varies with thickness, thicker layers often showing features not seen in thinner layers and which degrade its performance, such as graphitic inclusions, cracks and porosity. One cause of this is thought to be stress variation through the thickness of the layer, possibly directly related to the increase in grain size and the refinement of the orientation between grains.

c)   Marinelli et al only reports data at a single thickness of 115 μm. It is assumed by Marinelli et al that the layers produced by their method will follow the same trend with thickness seen in other materials, despite Marinelli et al claiming apparently very different behaviour (i.e. much higher collection efficiency) for it in its thin form. If the material is distinctly different, this trend would need to be proven in it. If this model is assumed to apply, there are further problems with Marinelli et al's data discussed later.

d)   at some point the grain boundaries will no longer be the limiting factor, and the increase in CCD with thickness will saturate at a maximum value dependent on the defects in the bulk of the diamond. Marinelli et al gives no insight where this limit lies in their material, further grounds for avoiding extrapolation. The poor quality of the bulk diamond in their samples is evident from the high degree of priming evident (see later).

Charge Collection Distance

The charge collection efficiency, η, as used in the present application is defined as:

$$\eta = \text{charge collected per event/charge generated per event} = Q_c/Q_g \qquad \text{Eq (1)}$$

this definition being well known in the art and is typically measured using beta (β) particles from a ^{90}Sr source, Q_g being well understood in such circumstances (36 electron-hole pairs per μm of diamond traversed, uniformly generated across the sample). Since it is not possible to collect more charge than is generated, η must lie between 0 and 1 (or 0% and 100%). Further, the charge collection distance d is related to η by:

$$d/D \approx (Q_c/Q_g), \text{ so } d \approx \eta.D \qquad \text{Eq (2)}$$

where D is the thickness of the detector. It should therefore be apparent that the value of d must satisfy the expression.

$$0 < d < D \qquad \text{Eq (3)}$$

It is also the case that d should be significantly less than D for the value of the d to have any real physical meaning as an absolute number rather than as a lower limit.

CCD can also be described in terms of more fundamental carrier properties:

$$CCD = (\mu_e + \mu_h)tE \qquad \text{Eq (4)}$$

where μ_e and μ_h are the hole and electron mobilities, t is the average carrier lifetime in the material and E is the applied field. Equation (4) can only reliably be used with Equation (2) when the carriers are uniformly generated through the thickness of the sample. If all the carriers are generated close to one surface, then one type of carrier (say holes) are collected as the time taken to drift to the surface is less than their lifetime, thus giving 100% collection of holes, whereas the other carrier (electrons) have to drift across almost the whole thickness of the detector with the consequent risk of being trapped or recombining.

This lack of symmetry means that great care is required in interpreting the raw collected charge data.

Marinelli et al uses alpha particles as a means of generating charge. Alpha particles have a very short penetration depth in diamond (between 10 and 15 µm), very high energies (5.5 MeV in the case of alphas from [241]Am) resulting in the generation of very large numbers of electron-hole pairs. The electron-holes are not generated uniformly along the track of the alpha particle, but are mostly generated close to the end of the track, known as the 'Bragg Peak' in the art.

Marinelli et al measures charge collection efficiency which is then converted to a charge collection distance using the Hecht equation, equation (3) in the paper. Marinelli et al states (in the 3 lines following equation) that equation (3) requires the electron-hole pairs to be uniformly generated over the penetration depth G of the alpha particle – this condition is not met by alpha particles, because of the Bragg Peak phenomena mentioned above, invalidating the basis of the data analysis.

There are three concerns then with using alpha particles. The first is that with alpha particles being fully absorbed in the sample, the signal from the diamond has to be used to trigger the charge recording/measuring apparatus (rather than the transiting particle triggering a separate independent detector in the case of beta irradiation). This means that there is no way of knowing when two (or more) alpha particles have arrived sufficiently closely together in time that the charge they generate is measured as a single pulse. There is no indication that this effect has been accounted for. Thus, it is likely that at least part of the efficiency curve is made up of events caused by two or more alpha particles, skewing the curve towards the high efficiency end of the scale.

The second concern is that the huge amount of charge generated by each alpha particle (about $5.5 \times 10^6/13.2 \approx 4.16 \times 10^5$ electron-hole pairs) in a very small volume rapidly causes polarisation effects to occur which affects the results often in an unpredictable way.

The third concern is how it affects the definition of CCD and whether the Hecht equation (equation 3 in Marinelli et al) can be applied without allowing for the non-uniform deposition of charge.

The actual measurement values reported by Marinelli et al are presented in a confusing manner and it is not surprising that at first reading there appear to be some very high values. In Figure 1 it appears that their detector shows a mean efficiency of ~50% and a maximum of ~70%, measured at a field of 40 kV/cm. In order for these values to be compared with other η values from the literature and to comply with the measurement method described in the specification of the above-identified application, they need to be scaled to a field of 10 kV/cm (i.e. 1 V/μm). Doing this using Figure 2, suggests a mean efficiency of closer to ~30%. If this figure is then converted to a charge collection distance using the relationship above, a value of $0.3 \times 115 = 35$ μm is obtained. This is the only CCD demonstrated by Marinelli et al which even partially conforms to the method defined in the specification of the above-identified application, and clearly falls well below the 150 μm threshold of the specification. All CCD values quoted above by Marinelli et al are either based on a higher applied field, or mere speculation based on technically unjustified extrapolation.

The measurement provided in Figure 1 of Marinelli et al, properly interpreted, shows a very poor uniformity in property, some areas having very low collection efficiency and others being much better (there are probably completely dead areas, but the triggering

technique means these cannot be included in the data, this again biases the data to artificially high values). Comparing the inset figure to the main figure is equally enlightening: in the text Marinelli et al states, 'It is well known that CVD diamond detectors must be pre-irradiated with ionising radiation ...... in order to achieve the highest detection efficiencies. This priming effect is qualitatively explained through a neutralisation of trapping defects by irradiation', (page 3217, column 1, paragraph 4). The average charge collection for the detector in the unprimed state (in the Figure 1 inset) is about 5%, this is hardly consistent with a 'high quality CVD diamond film' (page 3217, column 1, paragraph 1).

Marinelli et al's method of converting the values of η to CCD values using his equation 3 has produced values that are greater than the layer thickness (page 3217, column 2, paragraph 1), clearly in contravention of the discussion on the previous page, $0 < d < D$. This fundamental discrepancy casts further doubt on the validity of the measurements.

There are other technical deficiencies in the paper. For example, Marinelli et al reports (page 3216, column 2, last paragraph) on CVD polycrystalline diamond grown to 1 mm and then processed to 0.5 mm which shows a CCD of 250 μm, and then calculates this to be equivalent to a charge collection efficiency of 20%. Elementary math (and Equation (2) above) shows that since the charge collection distance is 50% of the thickness, then the charge collection efficiency is 50%.

Finally, whilst the paper and the examiner are focused on the highest values of collection efficiency observed in Figure 1, they do not provide a method to select these areas out from the areas of lowest charge collection efficiency to thereby provide a detector in any way similar to a single crystal diamond detector.
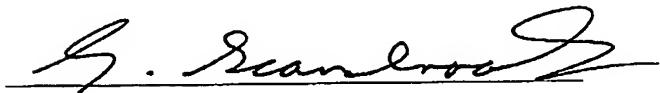
6. With regard to Marinelli et al combined with Vichr et al, Marinelli et al cannot be arbitrarily combined with Vichr et al to obtain a method of growing single crystal diamond which has a charge collection distance greater than 150 μm. In the first instance, one is a method of polycrystalline diamond growth, and grain boundaries can for example act as a sink for impurities and defects incorporated in the diamond, thus enhancing the properties of the volume of the grain, a mechanism not present in single crystal growth, so the method of Marinelli et al may not give the same electronic properties in single crystal growth. Furthermore, Marinelli et al discloses a method of producing a CCD of only 35 μm at an applied field of 10 kV/cm, and any value higher than this is speculation.

7. With regard to Marinelli et al combined with Vichr et al, and Plano et al, Plano et al discloses the use of an intermediate etch between growth steps during growth of a CVD diamond layer to remove defects present at the growth surface. Such defects would be point defects such as carbonaceous material. Plano et al does not disclose or suggest etching the substrate before the first stage of growth, to remove damage from the substrate surface caused during the preparation of that surface, and which causes dislocations to form in the layer. Once the dislocations are formed in the CVD layer, they thread through it and etching cannot remove them other than by etching back to the substrate and then further into the substrate in order to remove the damage at the surface of the substrate, which Plano et al does not disclose.

8. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that wilful false statements and the like so made

are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such wilful false statements may jeopardize the validity of the application or any patent issued thereon.

Signed at *Ascot* this *30th* day of *August* 2006

GEOFFREY ALAN SCARSBROOK